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A study of the electrical conductivity of the halogen doped trans-polyacetylene system $(CH)_x$, is reported. When films of trans-$(CH)_x$ are exposed to chlorine, bromine or iodine vapor, uptake of halogen occurs; and the conductivity increases markedly, over eight orders of magnitude in the case of iodine. The behavior of the halogenated polyacetylene is like that of a series of semiconductors with activation energies which vary with halogen content. The heavily doped polyacetylene shows metallic behavior with the semiconductor-metal transition near 2~3% dopant concentration. The results are discussed (over)

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19. (Cont'd)

impurities; intrinsic conductivity; activation energy; Ziegler
catalyst; matted fibrils; thermal isomerization; infrared spectrum;
$(CHI_{0.261})_x$; Electrodag; substituted polyethylene; $(CHI_{0.22})_x$;
dopant concentration; $(CHBr_y)_x$; $(CHI_y)_x$; residual defects; impurities;
insulating behavior; conductivity temperature dependence; acceptor;
donor.

20. (Cont'd)

In terms of a model of the doping process based on charge transfer.

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by

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CONDUCTING POLYMERS: HALOGEN DOPED POLYACETYLENE

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ABSTRACT

A study of the electrical conductivity of the halogen doped trans-polyacetylene system, $(CH)_x$, is reported. When films of trans-$(CH)_x$ are exposed to chlorine, bromine or iodine vapor, uptake of halogen occurs; and the conductivity increases markedly, over eight orders of magnitude in the case of iodine. The behavior of the halogenated polyacetylene is like that of a series of semiconductors with activation energies which vary with halogen content. The heavily doped polyacetylene shows metallic behavior with the semiconductor-metal transition near 2-3% dopant concentration. The results are discussed in terms of a model of the doping process based on charge transfer.

Introduction

Linear polyacetylene, $(CH)_x$, is one of the simplest conjugated organic polymers (Figure 1) and is therefore of special fundamental interest. From theoretical and spectroscopic studies of short chain polymers, the π-system transfer integral can be estimated as $\beta \simeq 2 - 2.5$ eV.[1] Thus the overall bandwidth would be of order 8-10 eV; $W = 2 z\beta$, where z is the number of nearest neighbors, β is the transfer integral and W is the bandwidth in the tight-binding approximation. The electrons from the unsaturated π-system are therefore delocalized along the polymer chains. However, because of the combined effects of bond alternation and Coulomb correlation, there is an energy gap in the excitation spectrum leading to semiconducting behavior. As a result of the large overall band width and unsaturated π-system, $(CH)_x$ is fundamentally different from either the traditional organic semiconductors made up of weakly interacting molecules (e.g., anthracene, etc.), or from other saturated polymers with monomeric units of the form $(\overset{R}{\underset{}{-}} C \overset{R'}{\underset{}{-}})$ where there are no π-electrons (e.g., polyethylene, etc.). Polyacetylene is therefore more nearly analogous to the traditional inorganic semiconductors; and indeed recent studies have shown that $(CH)_x$ can be chemically doped with a variety of donors or acceptors to give n-type or p-type semiconductors.[2,3,4,5,]

Early studies on this polymer system concentrated on the effort to produce pure material. Hatano et al.[6] found the electrical conductivity

depended on the crystallinity with higher crystallinity giving higher con-
ductivity. Berets and Smith[7] studied the effect of oxygen content on poly-
crystalline powder and found that oxygen in the polyacetylene did affect its
conductivity; the lowest oxygen content yielded the highest conductivity.
Their best samples had oxygen content as low as 0.7%. Shirakawa et al.[8]
pointed out that the room temperature conductivity of crystalline films of
polyacetylene depended on the cis-trans content varying from 10^{-5} $\Omega^{-1}\,cm^{-1}$
for the trans material to 10^{-9} $\Omega^{-1}\,cm^{-1}$ for the cis-isomer. In view of the
sensitivity of polyacetylene to impurities and/or defects as demonstrated
by the doping studies,[2-5] it appears likely that the intrinsic conductivity
of pure polyacetylene is even lower.

In this paper, we present a detailed report of our studies of the
effect of halogen doping on the electrical properties of polyacetylene. We
find that the electrical conductivity of halogen doped $(CH)_x$ can be syste-
matically increased by more than eight orders of magnitude. The associated
thermal activation energy decreases from initial values of about 0.3 eV to
near zero (~ 0.01 eV). The maximum room temperature conductivity for
iodine dopant exceeds 10^2 $\Omega^{-1}\,cm^{-1}$. Preliminary accounts of portions of
this work have been reported earlier.[2,3,4] The present paper is a more thorough
focussed study on the halogens as dopants in an attempt to develop an under-
standing of the nature of the doping process in this unusual class of semi-
conducting polymers.

Sample Preparation

Polyacetylene crystalline films were prepared using techniques[10] similar to those developed by Shirakawa[11,12] in the presence of a Zeigler catalyst. X-ray diffraction and scanning electron micrograph[11,12] studies show that films of any cis and trans composition are polycrystalline and consist of matted fibrils. As described by Shirakawa,[11,12] the measured density is 0.4 gm/cm^3 compared with 1.2 gm/cm^3 as obtained by flotation techniques, indicating that the polymer fibrils fill only about one-third of the film volume. This is shown clearly in electron micrographs obtained in our laboratory, in agreement with the earlier studies.[11,12] The cis-trans content was controlled by thermal isomerization.[8,11,12] Samples used in this study were 95-98% trans-polyacetylene as determined from their infrared spectrum; typical polymer films were approximately 0.1 mm in thickness. The studies presented here focus on the trans-$(CH)_x$, since this is the stable isomer at room temperature.

In general, upon doping the cis isomer appears to give consistently higher conductivity values (of order two to five times greater) than the trans isomer even though the trans isomer has a higher room temperature conductivity ($\sim 4 \times 10^{-5}$ ohm^{-1} cm^{-1}) than the cis isomer ($\sim 2 \times 10^{-9}$ ohm^{-1} cm^{-1}). Preliminary experiments suggest the same final product is obtained from both isomers when they are heavily doped and that the products are probably trans.[9]

4

Care was taken to achieve pure $(CH)_x$ starting material through extensive washing to remove all catalyst, with subsequent storage and handling in inert atmosphere to minimize oxygen content. Chemical analyses of typical cis and trans $(CH)_x$ films (before doping) are included in Table 1.

Halogen Doping Experiments

The halogen doping effect was demonstrated[2] by measuring the room temperature electrical conductivity while exposing the polymer film to a known pressure of halogen vapor. For example, in the case of iodine a pure $(CH)_x$ film was mounted in a glass vessel to which a bulb containing the halogen was attached. This iodine container was held at fixed temperature to produce a known vapor pressure of halogen. For bromine and chlorine, the pressure was monitored directly. The level of doping was determined by the vapor pressure and the time of reaction. The halogen content in the final product and at various stages in the reaction were determined from weight uptake and subsequently verified by chemical analysis. Typical analyses are given in Table 1.

Conductivity measurements were made without extensive pumping of the doped films. Experiments have shown that the change in conductivity is relatively insignificant when the films are held in a dynamic vacuum at room temperature. For example, the resistance of a film of composition $(CHI_{.061})_x$ was approximately doubled when its composition was converted

to $(CHI_{.163})_x$ after one hour of pumping. After three hours its composition

was essentially unchanged $[(CHI_{.178})_x]$; after four days it was $(CHI_{.147})_x$

and after nine days of continuous pumping a constant composition of

$(CHI_{.142})_x$ was obtained.[13] The iodine-doped films changed from their

characteristic lustrous silver color to shiny-black as the iodine was

removed. The color and conductivity were reversible on re-doping.

The on-line conductivity measurements as well as the temperature

dependence experiments utilized the standard four-probe technique. Due

to chemical activity of halogen, platinum leads and Electrodag were used

to make electrical contacts. Generally, the contacts were applied after

doping, in air with exposure time kept to a minimum (typically one-half

hour). However tests to check stability of the samples in air after doping

showed insignificant changes over the time periods involved; e.g., the

room temperature conductivity of $(CHI_{0.2})_x$ decreased by approximately

30% on exposure to air for 24 hours. The contacts were checked to be

ohmic. In addition to Electrodag, gold evaporated contacts and mechanical

(pressed) contacts have been tried. The various contacts yield conductivity

data which are consistent and without significant differences.

Fig. 2 and 3 illustrate the effect on the electrical conductivity

when trans-polyacetylene is doped with halogens. If the doping experiment

is carried out at a fixed pressure, the conductivity increases rapidly as

shown in Fig. 2; when polyacetylene is exposed to 1 torr of bromine vapor,

the conductivity increases by approximately a factor of 10^3 during the first

minute. The rate of change subsequently slows with σ approaching a maximum

value.

In the case of bromine and chlorine, continued reaction results in a slow decrease of the conductivity (as shown for Br in Figure 2). For bromine, the maximum conductivity corresponds to a concentration of about 5 mole % where σ has increased by approximately five orders of magnitude; see Fig. 4. Continued exposure results in an insulator containing more than 80% bromine.[14] Evidently the more reactive halogens add to the double bond; at the highest concentrations the results suggest the formation of a substituted polyethylene, $\left(\begin{array}{c} H \diagdown \diagup Br \\ -C- \end{array} \right)_x$, in which the π-system no longer exists.

The conductivity of the iodine doped polyacetylene approaches a saturation value after 24 hour reaction.[2] By careful control of the vapor pressure, the polymer can be doped to give any specified conductivity over eight orders of magnitude. The results from a controlled doping experiment are shown in Figure 3. The initial increase is more than six orders of magnitude; further increase in concentration raises the conductivity another factor of ten. At the highest concentration, the composition $(CHI_{0.22})_x$ has an average conductivity of approximately $10^2 \, \Omega^{-1}\text{-}cm^{-1}$ with values ranging from $30 \, \Omega^{-1}\text{-}cm^{-1}$ to $160 \, \Omega^{-1}\text{-}cm^{-1}$ depending on the detailed vapor pressure and reaction rate during doping. A slower rate generally appears to yield a higher conductivity value suggesting that inhomogeneous doping may result if the reaction is carried out too rapidly. As noted above cis-$(CH)_x$ films give higher conductivities than films formed by doping

trans-$(CH)_x$. Thus, lustrous silvery films of $(CHI_{0.28})_x$ have been obtained from cis-$(CH)_x$ with room temperature conductivities > 500 $(\Omega\text{-cm})^{-1}$. After doping a film to saturation at the composition $(CHI_{0.22})_x$, the sample cell was subsequently pumped out, and the sample kept in vacuum for two days. During this period, the conductivity remained high; decreasing only about 30% in the two day period under vacuum.

The room temperature conductivity of bromine and iodine doped $(CH)_x$ is shown in Figure 4 as a function of dopant concentration. In this series of measurements, each sample was prepared from the same batch of starting material, trans-$(CH)_x$, and doped with various concentrations of dopant. The room temperature conductivity was subsequently measured in air, and the composition was determined by weight increase. It should be noted that in the case of bromine, if doping is stopped in the high conductivity regime (e.g., after 20 minutes in Fig. 2), no subsequent addition of the bromine in the doped material to the double bond occurs. Addition only takes place in the presence of excess bromine. In the case of iodine, no addition occurs even in the presence of excess halogen.

Temperature Dependence of the Electrical Conductivity

The conductivities of samples of polyacetylene doped with various concentrations of bromine and iodine were measured as a function of temperature. The results are shown in Fig. 5 and 6 for $(CHBr_y)_x$ and $(CHI_y)_x$,

respectively. The temperature range covered by the measurements depended on the resistance of the sample; for the highest conductivity sample, data were obtained over the entire range from 300 K to 3 K. In general, we find that the conductivity of halogen doped polyacetylene decreases with decreasing temperature. However, the plots of $\ln\sigma$ vs. $1/T$ do not give straight line behavior as seen in Fig. 5 and 6. Plotting the data as $\ln\sigma$ vs. $T^{-\frac{1}{4}}$ (or $T^{-\frac{1}{2}}$) tends to give more nearly straight line behavior as shown in Fig. 7a, 7b.

The general behavior shown on Fig. 5 and 6 is toward smaller activation energy as the dopant concentration increases. We use the initial slope of the $1/T$ plots to determine the approximate thermal activation energy, E_o, which serves as a simple index of the conductivity behavior. The resulting activation energies are shown in Figure 8 as a function of concentration y for both $(CHBr_y)_x$ and $(CHI_y)_x$. Undoped polyacetylene has an activation energy in the range from 0.3 eV (trans) to 0.5 eV (cis).[8] However, the compensation experiments indicate that the conductivity in the undoped polymer results from residual defects and/or impurities.[2,4,5] Thus the intrinsic $(CH)_x$ activation energy is probably significantly higher. On doping with halogen, the activation energy drops rapidly reaching a value as low as 0.018 eV at about 20 mole % iodine. Similar results are obtained from bromine doping. In the latter case, $E_o(Br)$ goes through a minimum value of 0.046 eV at about 5 at. %, increasing at high bromine content with insulating behavior observed in the fully brominated compound.

The rapid initial decrease in E_o stops at a concentration $y \sim 0.02$ for both systems. At higher values (Fig. 8), E_o is small and only weakly dependent on concentration. This sharp change in behavior at $y \sim 0.02$ can also be seen in the room temperature conductivity data, Fig. 4, for both systems.

Three samples of the high conductivity polymer $(CHI_{0.22})_x$ were studied from 300 K to 3 K. Figure 9 shows the temperature dependence of $(CHI_{0.22})_x$ over the full temperature range. The average activation energy obtained from the interval 300 K - 100 K is $(1.37 \pm 0.07) \times 10^{-2}$ eV. At low temperature (3 K - 10 K) the average activation energy is $(1.0 \pm 0.2) \times 10^{-3}$ eV. Figure 10 shows the temperature dependence of one of the high conductivity $(CHI_{0.22})_x$ samples plotted linearly as σ vs. T. Although the conductivity decreases with decreasing temperature, it clearly is not activated. Similar results were obtained earlier for samples heavily doped with AsF_5. However, if cis-(CH)$_x$ films are doped with AsF_5 after the electrical contacts are attached to the film, a significantly higher room temperature conductivity (by a factor of two to three) is obtained than when the contacts are applied after doping. Furthermore, as the temperature is lowered, the conductivity goes through a maximum; a small but definite increase in conductivity, followed by a decrease, is observed in the former case ($\sigma_{200 K}/\sigma_{300 K} = 1.05$ at approximately 200 K).[15] Figures 9 and 10 indicate that a semiconductor picture with

a single activation energy is inadequate to describe the high conductivity regime, consistent with the earlier observation of a semiconductor-metal transition at high doping levels.

Discussion

The sudden change in the concentration dependence of the conductivity and the activation energy near $y = 0.02$ is consistent with a semiconductor-to-metal transition near the 2% dopant level, in agreement with earlier far infrared and transport studies.[3] The temperature dependence studies indicate that samples with $y < 0.02$ show an activated conductivity with the activation energy being a strong function of dopant concentration. For $y > 0.02$, the activation energy is sufficiently small that interfibril contacts in the polycrystalline polymer films may be playing a limiting role. In fact, the value of $\sigma(300 \text{ K}) \geq 10^2 (\Omega\text{-cm})^{-1}$ found for $(CHI_{0.22})_x$ is greater than typically found for $(SN)_x$ films[16-19] (reported values range from $10 (\Omega\text{-cm})^{-1}$ to $60 (\Omega\text{-cm})^{-1}$ depending upon substrate conditions), $(SN)_x$ polycrystalline compactions[16-19] ($\sigma \simeq 30 \ \Omega^{-1} \text{ cm}^{-1}$), or polycrystalline compactions of TTF-TCNQ[20] ($\sigma \simeq 15 \ \Omega^{-1}\text{-cm}^{-1}$).

The behavior of the conductivity as a function of temperature shown in Figures 5, 6, 7, and 9 is qualitatively similar to that found for films of $(SN)_x$ where the temperature dependence has been attributed to interparticle contact.[16-19] Studies of the temperature dependence of the conductivity of polycrystalline $(SN)_x$[16-19] and organic conductors such as TTF-TCNQ[20]

often show activated behavior even though the single crystal data indicate metallic behavior. The low apparent activation energy and high room temperature conductivity of doped polyacetylene suggest that this may be the case in these systems as well. Straight line behavior for plots of $\ln\sigma$ vs. $T^{-1/(d+1)}$ is often taken as indicative of variable range hopping[21] in three dimensions (d = 3) or one-dimension (d = 1). Although the temperature dependence is approximately of this form (see Fig. 7), the electron microscopy results suggest that the inter-fiber contact is the dominant effect.

Raman studies[22,23] of iodine doped polyacetylene have recently identified the presence of I_3^- in the metallic polymer. Based on this observation, the demonstration of stoichiometric compensation of sodium-doped films with iodine,[5] the observation that iodine can be partially removed from the more heavily-doped films through the use of a suitable solvent such as n-pentane or by pumping[9] and the analogy with graphite intercalation,[24] we believe the doping of $(CH)_x$ results from charge transfer. Charge transfer occurs from polymer to acceptor (A) with the polymer chain acting as a polycation in the presence of an A^- species (in the case of iodine, primarily I_3^-). For a donor (D), the polymer chains act as a polyanion in the presence of D^+ species. The A^- or D^+ ions reside between polymer chains and/or on the surface of the polymer fibres. The charge transfer need not be complete. The resulting electron (or hole) on the polymer chain is weakly bound to the D^+ (or A^-) ions by the Coulomb

potential, forming donor (or acceptor) states in the gap. At low levels, thermal activation out of the bound states results in carriers for transport along the polymer chain. Above approximately 2% doping, the bound states are screened,[3] and the carriers are free to move along the polymer chains resulting in metallic behavior.

In the case of the more reactive halogens, bromine and chlorine, the situation is evidently more complicated. The doping experiments indicate that bromine attacks the π-system at least at high concentrations and actually adds to the double bonds. These results suggest that for optimum transport properties, a dopant should give charge transfer with the A^- ion (acceptor) or D^+ ion (donor) between chains but not involved in a direct chemical bond to the polymer chain. This charge transfer doping gives excess carriers without disruption of the delocalized π-system, thus leading to relatively high mobility.

In summary, we have shown that halogen doped polyacetylene forms a class of conducting polymers in which the electrical conductivity can be systematically and continuously varied over a wide range. The associated thermal activation energy decreases with halogen doping. The properties of the high conductivity compositions are suggestive of metallic behavior in which the transport is limited by interparticle contact in the polycrystalline films. Studies of the effects of different halogens have provided insight into the nature of the doping process in this novel organic polymer.

References:

1. For a summary of these data and detailed references see A. A. Ovchinnikov, Sov. Phys. Uspekhi $\underline{15}$, 575 (1973)

2. H. Shirakawa, E. J. Louis, A. G. MacDiarmid, C. K. Chiang, and A. J. Heeger, Chem. Comm. 578 (1978)

3. C. K. Chiang, C. R. Fincher, Jr., Y. W. Park, A. J. Heeger, H. Shirakawa, E. J. Louis, S. C. Gau and A. G. MacDiarmid, Phys. Rev. Lett. $\underline{39}$, 1098 (1978)

4. C. K. Chiang, M. A. Druy, S. C. Gau, A. J. Heeger, E. J. Louis, A. G. MacDiarmid, Y. W. Park, J. Am. Chem. Soc. $\underline{100}$, 1013 (1978)

5. C. K. Chiang, S. C. Gau, C. R. Fincher, Jr., Y. W. Park, A. G. MacDiarmid and A. J. Heeger, Appl. Phys. Letters (in press)

6. M. Hatano, S. Kambara, S. Okamoto, J. Polym. Sci. $\underline{51}$, 526 (1961)

7. D. J. Berets and D. S. Smith, Trans. Faraday Soc. $\underline{64}$, 823 (1968)

8. H. Shirakawa, T. Ito, S. Ikeda, Die Macromoleculare Chemie (in press)

9. H. Shirakawa, (Private communication); M. Ozaki, A. J. Heeger and A. G. MacDiarmid, unpublished observations (1978)

10. S. C. Gau, Y. Matsumura, M. Druy and A. G. MacDiarmid, to be published

11. T. Ito, H. Shirakawa and S. Ikeda, J. Polym. Sci. Polym. Chem. Ed. $\underline{12}$, 11 (1974); $\underline{13}$, 1943 (1975)

12. H. Shirakawa, T. Ito and S. Ikeda, Polym. J. $\underline{4}$, 460 (1973); H. Shirakawa and S. Ikeda, Polym. J. $\underline{2}$, 231 (1971)

13. A. Pron, A. G. MacDiarmid and A. J. Heeger, unpublished observations (1978)

14. H. Shirakawa (Private communication)

15. S. C. Gau, Y. W. Park, A. J. Heeger and A. G. MacDiarmid, unpublished observations (1978)

16. A. A. Bright, M. J. Cohen, A. F. Garito and A. J. Heeger, Appl. Phys. Letters $\underline{26}$, 612 (1975)

17. M. M. Labes, Pure Appl. Chem. $\underline{12}$, 275 (1966); see also M. J. Cohen, Ph. D. Thesis, University of Pennsylvania, Phila. Pa. (1975)

18. F. de la Cruz and H. J. Stoltz, Sol. State Commun. $\underline{20}$, 241 (1976); R. J. Soulen and D. B. Utton, Sol. State Commun. $\underline{21}$, 105 (1977)

19. W. D. Gill, W. Boyer and G. B. Street, Bull. Am. Phys. Soc. $\underline{22}$, #3, 372 (1977)

20. L. B. Coleman, Ph. D. Thesis, University of Pennsylvania, Phila., Pa. (1975)

21. N. F. Mott, Phil. Mag. $\underline{19}$, 835 (1969); N. F. Mott, Festkörper-probleme $\underline{9}$, 22 (1969); V. Ambegrokar, B. I. Halperin and J. S. Langer, Phys. Rev. B $\underline{4}$, 2612 (1971)

22. S. L. Hsu, A. J. Signorelli, G. P. Pez and R. H. Baughman, J. Chem. Phys. (in press)

23. H. Shirakawa and S. Ikeda (to be published)

24. Proceedings of the International Conference on Intercalation Compounds of Graphite, Mat. Sci. Eng. $\underline{31}$, (December 1977)

TABLE 1
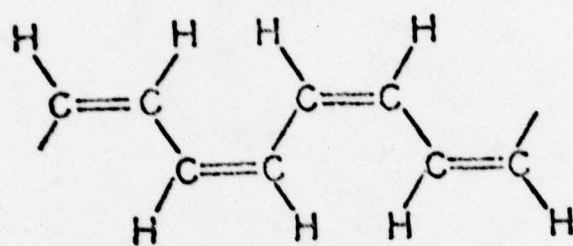
Chemical Analysis of Pure and Doped $(CH)_x$ [a]

		C%	H%	Halogen%	Total
1) $(CH)_x$	calculated	92.26	7.74		100.00
cis-$(CH)_x$	found	92.16	7.81		99.97
trans-$(CH)_x$	found	92.13	7.75		99.88
2) trans-$(CHI_{0.22})_x$ [b]	calculated	29.34	2.46	68.20	100.00
	found	29.14	2.62	68.26	100.02
3) trans-$(CHBr_{0.224})_x$ [b]	calculated	38.85	3.26	57.89	100.00
	found	38.89	3.05	58.16	100.10

[a] Galbraith Laboratories, Inc.

[b] The designation "trans" refers to the isomeric form of the $(CH)_x$ employed in the doping experiment. It does not necessarily imply that the doped material has the same isomeric composition as the original $(CH)_x$.
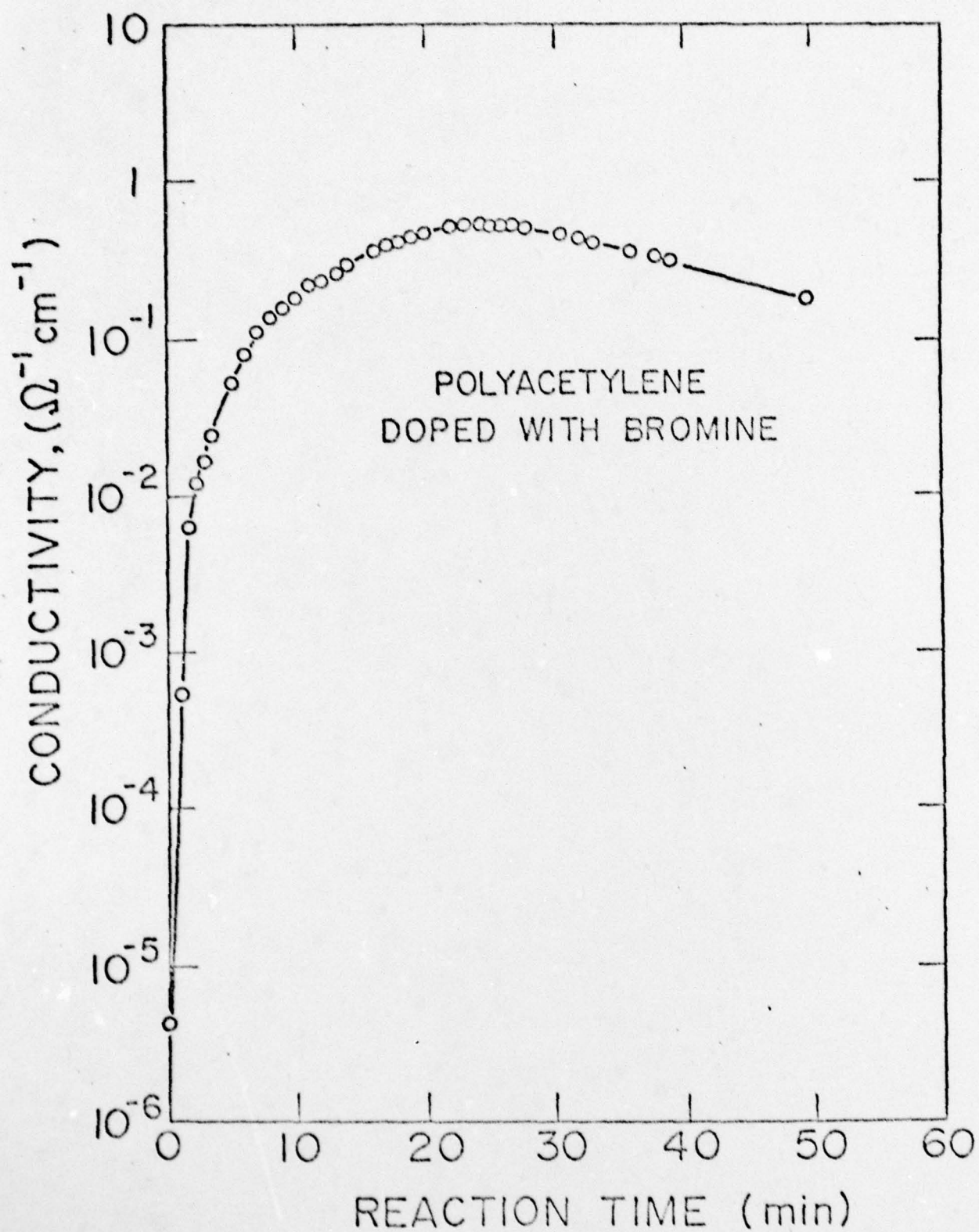
Figure Captions:

Figure 1: Chemical structure of polyacetylene; the cis and trans isomers are shown.

Figure 2: Electrical conductivity (4-probe) of trans-$(CH)_x$ during doping reaction with bromine.

Figure 3: Electrical conductivity (4-probe) of trans-$(CH)_x$ during doping reaction with iodine. The conductivity is normalized to that of the undoped sample.

Figure 4: Electrical conductivity of halogen doped polyacetylene as a function of bromine and iodine concentration.

Figure 5: $\ln \sigma$ vs. $1/T$ for $(CHBr_y)_x$ with various concentrations (y) of bromine.

Figure 6: $\ln \sigma$ vs. $1/T$ for $(CHI_y)_x$ for various concentrations (y) of iodine

Figure 7a: $\ln \sigma$ vs. $1/T^{\frac{1}{4}}$ for $(CHBr_y)_x$ with various concentrations (y) of bromine.

Figure 7b: $\ln \sigma$ vs. $1/T^{\frac{1}{4}}$ for $(CHI_y)_x$ with various concentrations (y) of iodine.

Figure 8: Activation energy of halogen doped polyacetylene as a function of concentration. The activation energies were obtained from the slopes of the curves in Figures 5 and 6.

Figure 9: Resistivity of $(CHI_{0.22})_x$ plotted as $\ln \rho$ vs. $1/T$ over the full range from 300 K to 3 K.

Figure 10: Temperature dependence of the normalized conductivity for two concentrations of $(CHI_y)_x$.

     y = 0 (undoped) o ● o (below metal-insulator transition)
     y = 0.22   o o o (above metal-insulator transition)

CIS

TRANS

POLYACETYLENE
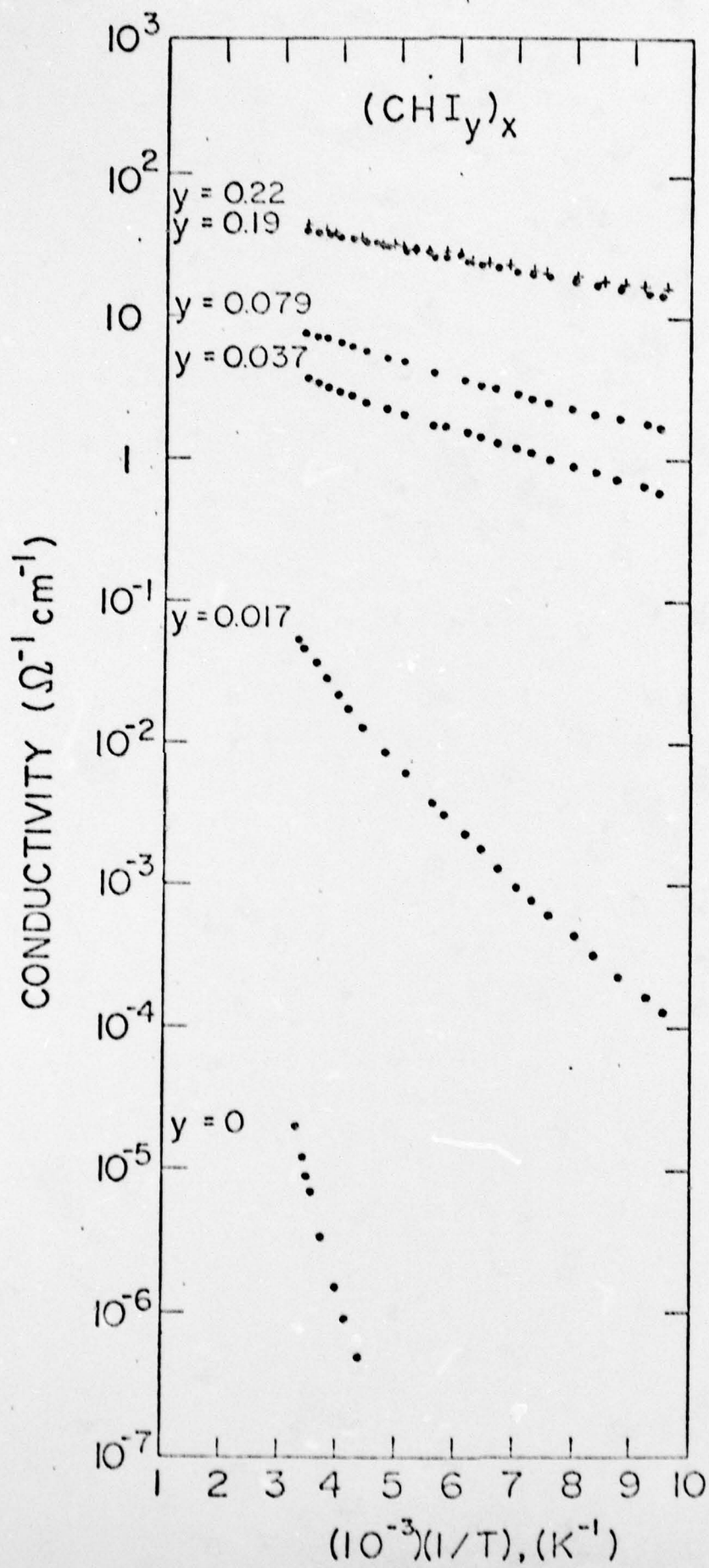DOPED WITH BROMINE

Figure showing CONDUCTIVITY ($\Omega^{-1} cm^{-1}$) versus $(10^3)(1/T)$, (K^{-1}) for $(CHBr_y)_x$ with curves labeled $y = 0.195$, $y = 0.0141$, $y = 0.0057$, $y = 0.0029$, and $y = 0$.
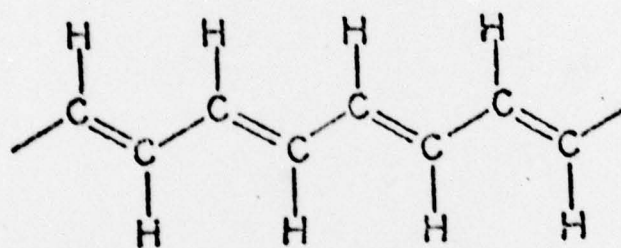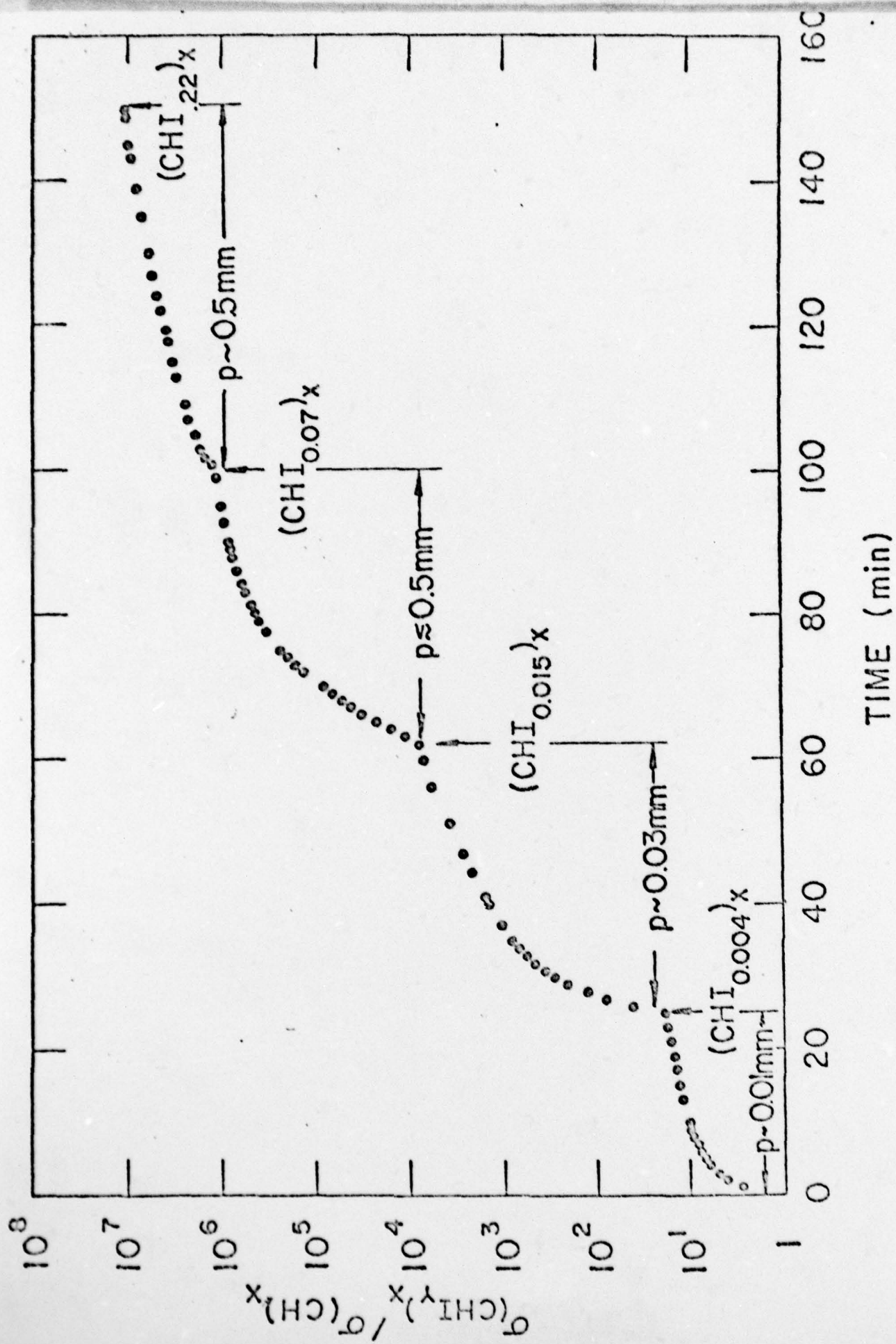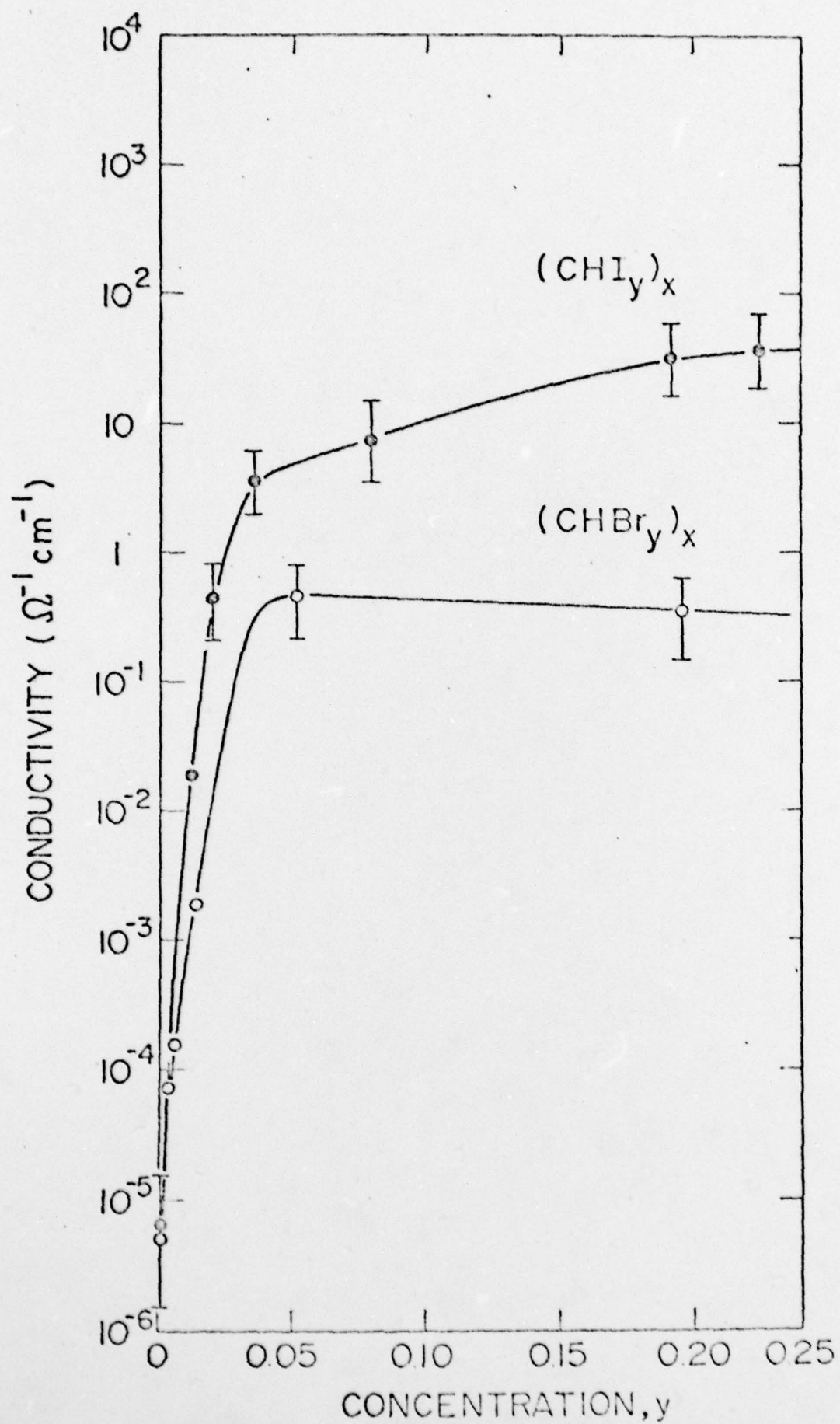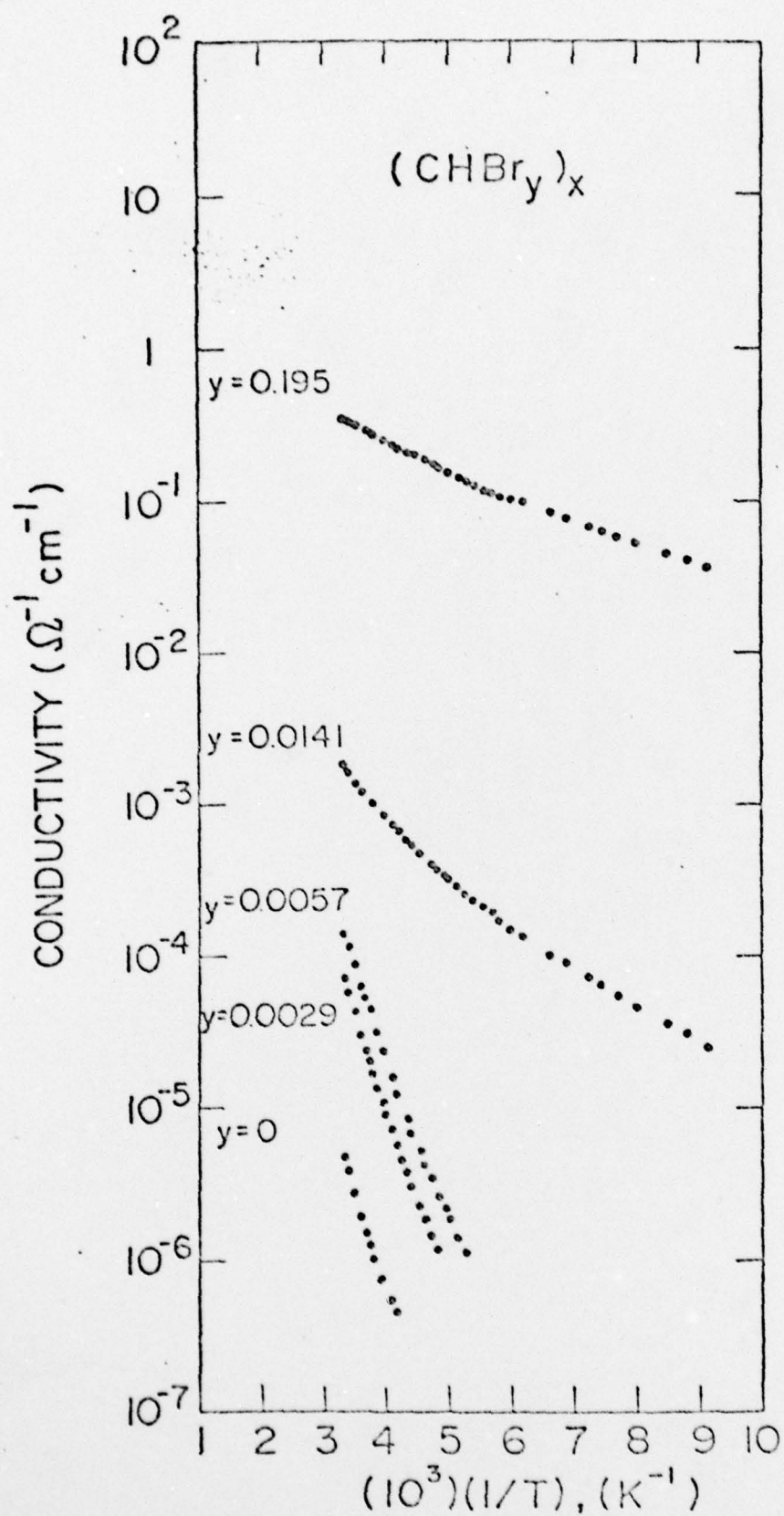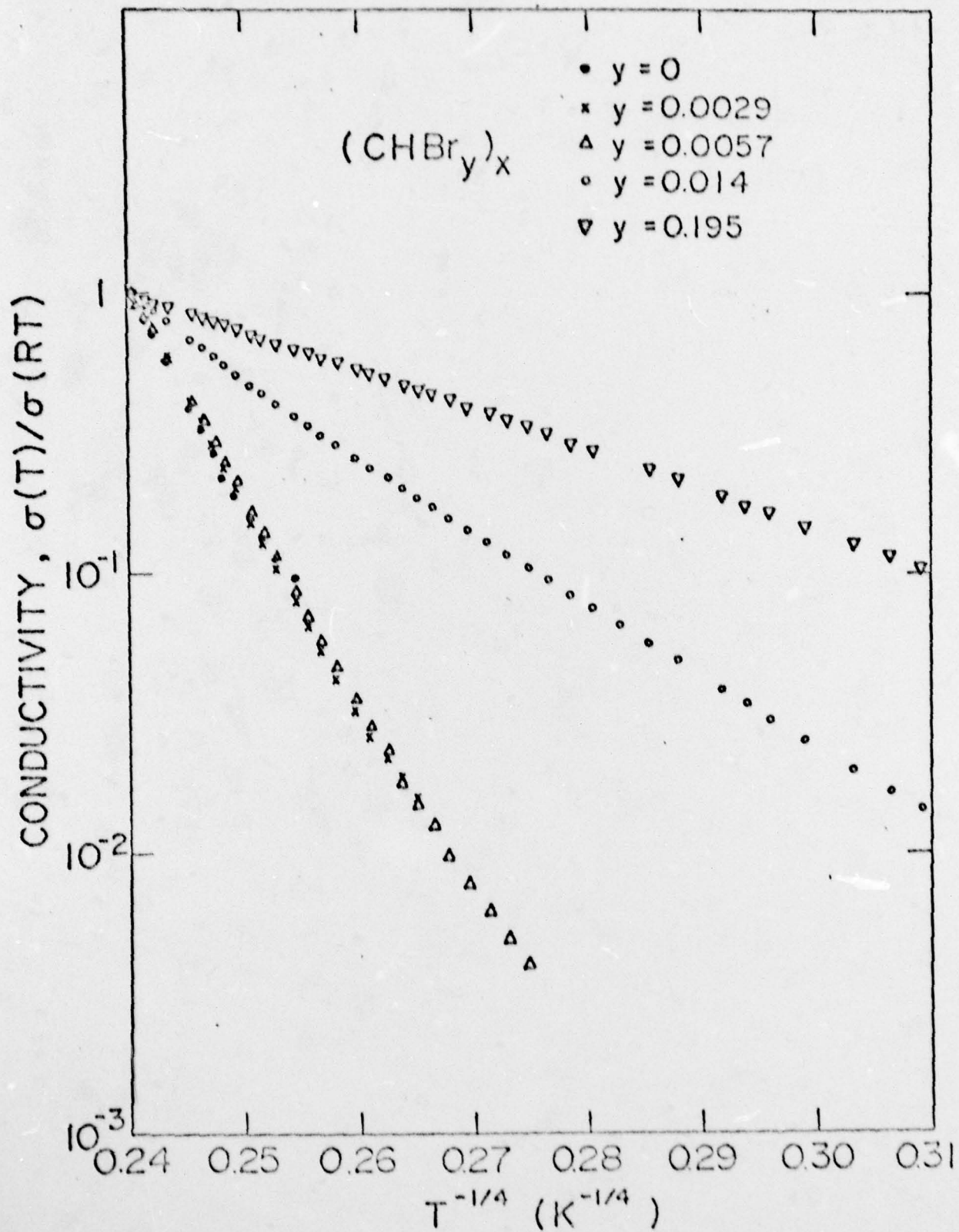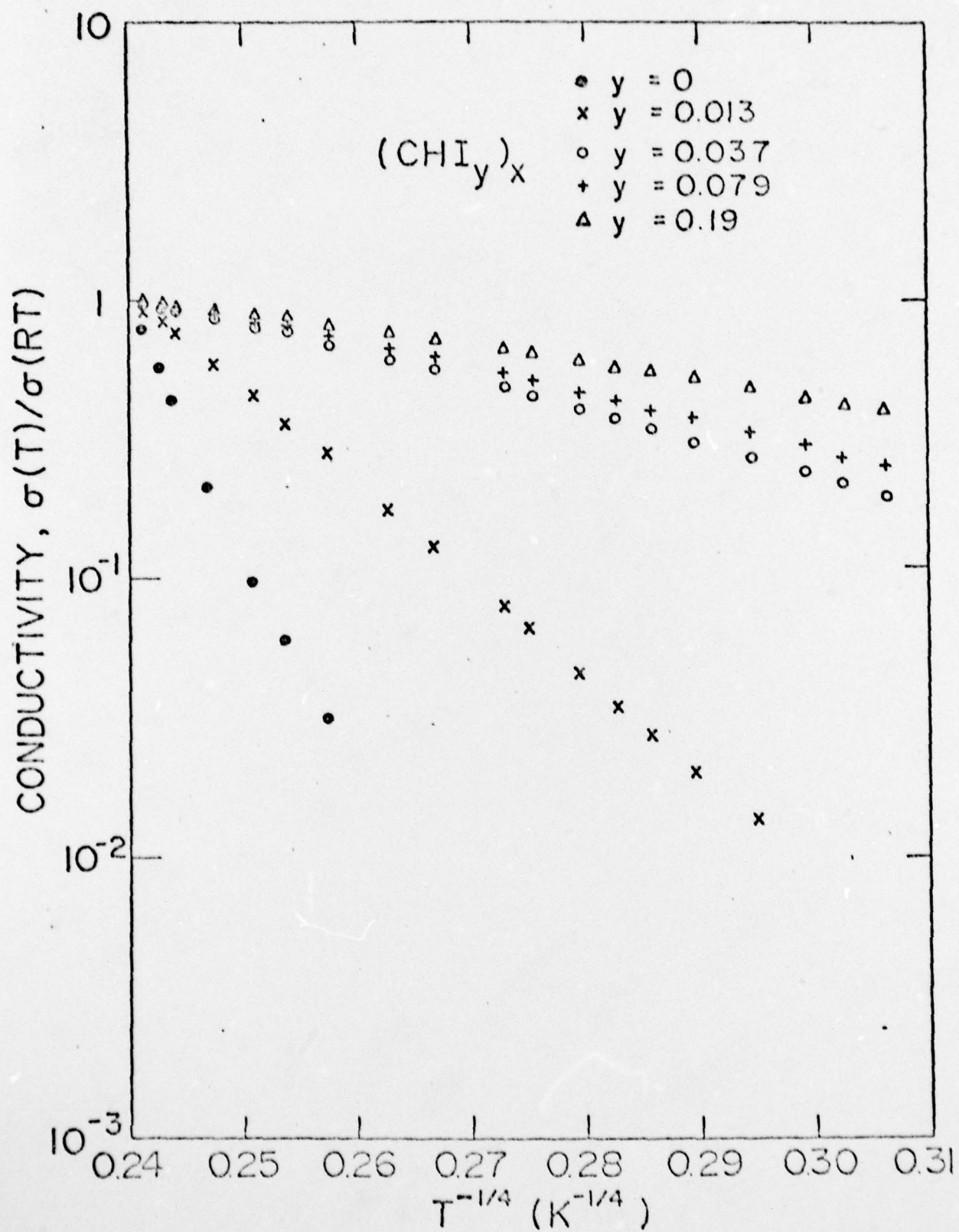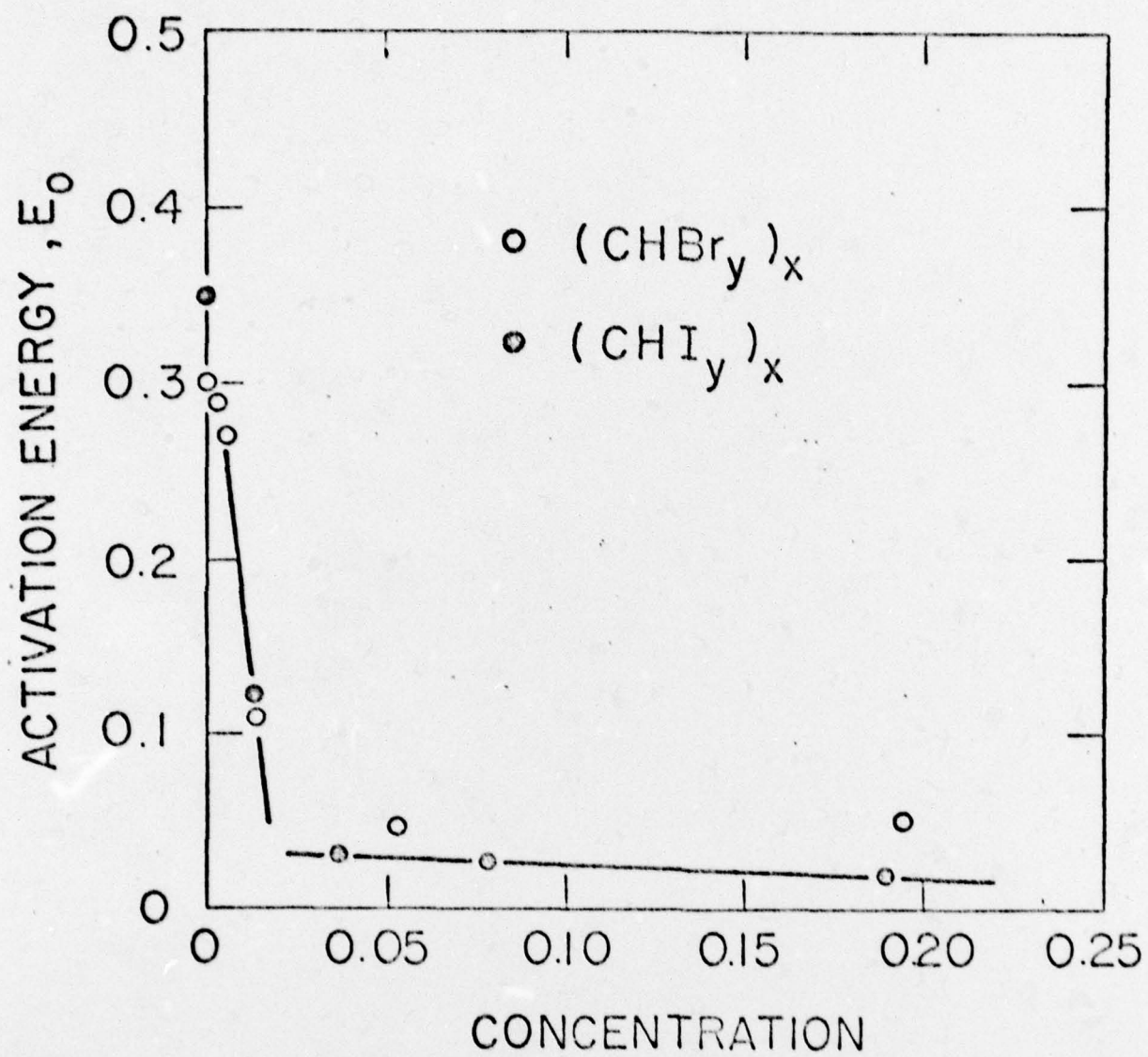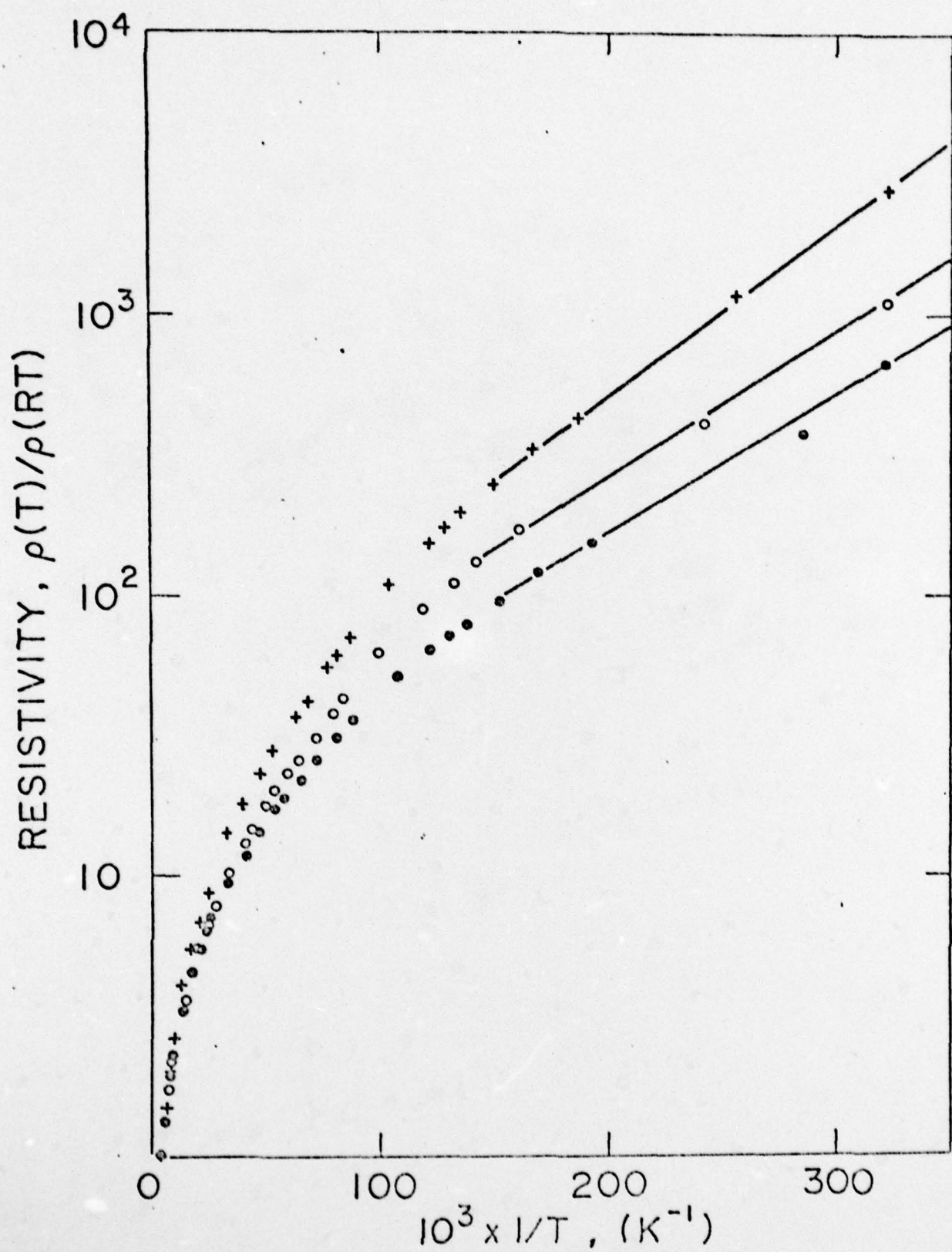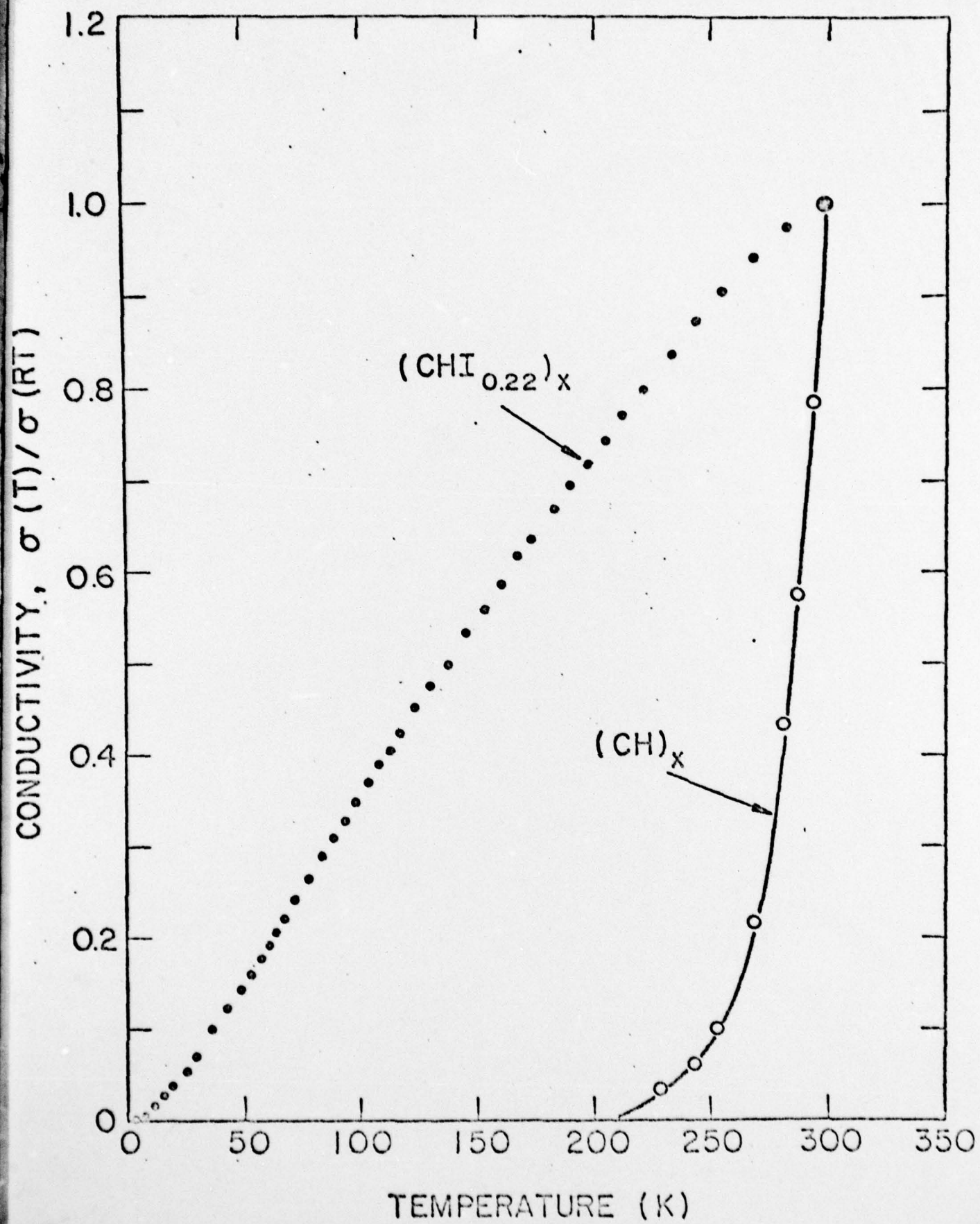
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